

## Claims:

*Sub A2*

1. A composite of a vulcanizable rubber or rubber-type composition having at least one metal reinforcement element embedded therein, wherein said metal reinforcement elements have a coating of a polymer deposited from a solution and are compatible with and co-polymerizable with said vulcanizable rubber composition, and bearing functional groups covalently bonding to the metal surface of said reinforcement element.

10 2. A composite according to claim 1, wherein said solution is an aqueous solution.

15 3. A composite according to claim 1, wherein said solution is an alcoholic solution.

4. A composite according to claim 1, wherein said solution is an organic solution.

20 5. A composite according to claim 1, wherein said metal reinforcement elements have a coating of a non-cured rubber composition.

6. A composite according to claim 1, wherein said metal reinforcement elements are co-vulcanizable with said vulcanizable rubber composition.

25 7. A composite according to claim 1, wherein said metal reinforcement elements are crosslinkable with said vulcanizable rubber composition.

5 8. A composite according to claim 1, wherein said functional groups form covalent bonds with the outward directed first functional groups of a molecular layer of a bifunctional adhesion promoter which is intercalated between said metal reinforcement elements and said coating and is bound to said metal reinforcement elements by its second functional groups.

10 9. A composite according to claim 1, wherein said metal reinforcement elements comprise on top of said coating, a layer of a skim composition for the vulcanizable rubber or rubber-like composition.

15 10. A composite according to claim 1 wherein the vulcanizable rubber composition to be reinforced is a composition selected from the group consisting of a synthetic poly(isoprene), a natural poly(isoprene), a synthetic poly(butadiene), natural poly(butadiene), a styrene-butadiene-rubber (SBR), a halobutylrubber, or an ethylene-propylene-diene-rubber (EPDM).

20 11. A composite according to claim 1, wherein said metal reinforcement element is an elongated steel element.

25 12. A composite according to claim 11, wherein said elongated steel element is coated with at least one metallic layer.

30 13. A composite according to claim 12, wherein said metallic layer is comprised of a metal selected from the group consisting of brass, bronze, zinc, zinc alloy, tin or tin alloy.

14. A composite according to claim 13, wherein said zinc alloy is an alloy selected from the group consisting of a zinc-aluminium alloy, a zinc-aluminium-mischmetal alloy, a zinc-manganese alloy, a zinc-cobalt alloy, a zinc-nickel alloy, a zinc-iron alloy or a zinc-tin alloy.

5 15. A composite according to claim 5, wherein said non-cured rubber composition is comprised of matter selected from the group consisting of a synthetic poly(isoprene), a natural poly(isoprene), a synthetic poly(butadiene), a natural poly(butadiene), a synthetic elastomer or a thermoplastic elastomer.

10 16. A composite according to claim 1 wherein said polymer bonds directly to the metal surface and has functional groups selected from the group consisting of:

10      thiol groups, mercapto groups, silanes, amines,  
-SH; -SiHCl<sub>2</sub>; -SiH<sub>2</sub>Cl; -Si(Cl)<sub>3</sub>; -SiHBr<sub>2</sub>; -SiH<sub>2</sub>Br; -SiBr<sub>3</sub>; -Si(R'(Cl)<sub>2</sub>);  
-Si(OR')<sub>3</sub>; -Si(R'(OR')<sub>2</sub>); -COOH; -COCl;  
-PO<sub>3</sub>H<sub>2</sub>, -SO<sub>2</sub>H,  
acid anhydrides of -SH; -SiHCl<sub>2</sub>; -SiH<sub>2</sub>Cl; -Si(Cl)<sub>3</sub>; -SiHBr<sub>2</sub>; -SiH<sub>2</sub>Br; -  
15 SiBr<sub>3</sub>; -Si(R'(Cl)<sub>2</sub>); -Si(OR')<sub>3</sub>; -Si(R'(OR')<sub>2</sub>); -COOH; -COCl;  
-PO<sub>3</sub>H<sub>2</sub>, -SO<sub>2</sub>H,  
acid chloride groups of -SH; -SiHCl<sub>2</sub>; -SiH<sub>2</sub>Cl; -Si(Cl)<sub>3</sub>; -SiHBr<sub>2</sub>; -SiH<sub>2</sub>Br;  
-SiBr<sub>3</sub>; -Si(R'(Cl)<sub>2</sub>); -Si(OR')<sub>3</sub>; -Si(R'(OR')<sub>2</sub>); -COOH; -COCl;  
-PO<sub>3</sub>H<sub>2</sub>, -SO<sub>2</sub>H,  
20 organometallic groups of the formula -M(OR')<sub>n</sub>, whereby M is a metal selected from the group consisting of Al, Sn, B, Ti and V; and n is the ligand number corresponding to the metal M; and  
a phthalocyanin, phthalonitril groups, a monothiol, or monothiolate groups; and R' is an alkyl selected from the group consisting of methyl, ethyl or  
25 propyl.

17. A composite according to claim 1 wherein said polymer bonds to the intercalated adhesion promoter and has functional groups comprising thiol groups, mercapto groups, silanes, amines,

5 -SH; -SiHCl<sub>2</sub>; -SiH<sub>2</sub>Cl; -Si(Cl)<sub>3</sub>; -SiHBr<sub>2</sub>; -SiH<sub>2</sub>Br; -SiBr<sub>3</sub>; -Si(R'(Cl)<sub>2</sub>); -Si(OR')<sub>3</sub>; -Si(R'(OR')<sub>2</sub>); -COOH; -COCl;

-PO<sub>3</sub>H<sub>2</sub>, -SO<sub>2</sub>H,

acid anhydride groups of -SH; -SiHCl<sub>2</sub>; -SiH<sub>2</sub>Cl; -Si(Cl)<sub>3</sub>; -SiHBr<sub>2</sub>; -

SiH<sub>2</sub>Br; -SiBr<sub>3</sub>; -Si(R'(Cl)<sub>2</sub>); -Si(OR')<sub>3</sub>; -Si(R'(OR')<sub>2</sub>); -COOH; -COCl;

-PO<sub>3</sub>H<sub>2</sub>, -SO<sub>2</sub>H,

10 acid chloride groups of -SH; -SiHCl<sub>2</sub>; -SiH<sub>2</sub>Cl; -Si(Cl)<sub>3</sub>; -SiHBr<sub>2</sub>; -SiH<sub>2</sub>Br;

-SiBr<sub>3</sub>; -Si(R'(Cl)<sub>2</sub>); -Si(OR')<sub>3</sub>; -Si(R'(OR')<sub>2</sub>); -COOH; -COCl;

-PO<sub>3</sub>H<sub>2</sub>, -SO<sub>2</sub>H,

a phthalocyanin, phthalonitril groups, a monothiol, or monothiolate groups;

wherein R' is an alkyl selected from the group consisting of methyl, ethyl

15 or propyl; and

said functional groups are terminal groups.

18. A composite according to claim 17, wherein said functional groups are carried along a polymer backbone.

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19. A composite according to claim 17, wherein said functional groups are part of side chains of the polymer.

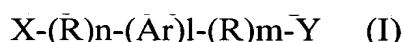
25 20. A composite according to claim 18, wherein said functional groups are epoxy groups carried along the polymer backbone.

21. A composite according to claim 18, wherein said functional groups are epoxy groups which are part of side chains attached to the polymer backbone.

22. A composite according to claim 16, wherein said organometallic groups are of the formula  $-M(Cl)_n$ ,

23. A composite according to claim 5, wherein said non-cured rubber composition comprises common vulcanization additives and curing systems.

24. A composite according to claim 1, wherein said polymer is bound to said metal surface by an adhesion promoter that is a bifunctional compound of the general formula (I)



with X representing a group capable of reacting covalently at the metal surface,

R representing an organic spacer chain,

Ar representing an aromatic system,

Y representing a group capable of forming covalent bonds to the functional groups of said coating, and  $0 \leq n, m \leq 16$ ; and  $0 \leq l \leq 6$ .

25. A composite according to claim 24, wherein A represents a heteroaromatic system.

26. A composite according to claim 24 wherein

X is a functional group selected from the group consisting of -SH;  $-SiHCl_2$ ;  $-SiH_2Cl$ ;  $-Si(Cl)_3$ ;  $-SiHBr_2$ ;  $-SiH_2Br$ ;  $-SiBr_3$ ;  $-Si(R'(Cl)_2$ );  $-Si(OR')_3$ ;  $-Si(R'(OR')_2$ ); -COOH; -COCl;  $-PO_3H_2$ ;  $-SO_2H$ ; an organometallic group of the formula  $-M(OR')_n$ , whereby M is a metal selected from the group consisting of Al, Sn, B, Ti and V and n is the ligand number corresponding to the metal M; a phthalocyanin; a phthalonitril group; a monothiol; or a monothiolate group;

R' is an alkyl

Y is a functional group selected from the group consisting of  $\text{NH}_2$ ;  $\text{NHR}'$ ;  $\text{NR}_2$ ; an unsaturated residue; an acrylic acid group; a methacrylic acid group; methyl esters or ethyl esters;

-CN is a functional group selected from the group consisting of an activated carboxylic ester; an aldehyde group; an epoxide group; -SH; -SiHCl<sub>2</sub>; -SiH<sub>2</sub>Cl; -Si(Cl)<sub>3</sub>; -SiHBr<sub>2</sub>; -SiH<sub>2</sub>Br; -SiBr<sub>3</sub>; -Si(R'(Cl)<sub>2</sub>); -Si(OR')<sub>3</sub>; -Si(R'(OR')<sub>2</sub>); -COOH; -COCl; or a functional group capable of forming a complex with at least one ingredient of a non-metallic medium;

R represents -CH<sub>2</sub>-; and

AR represents an aromatic system.

27. A composite according to claim 26, wherein AR represents a heteroaromatic system.

28. A composite according to claim 26, wherein R represents a -(CH<sub>2</sub>)<sub>n</sub> chain;  $2 \leq n \leq 20$ ; and said chain may be unhalogenated, may contain aromatic units, and may comprise constituents selected from the group consisting of: -(CH<sub>2</sub>)<sub>i</sub>CH<sub>3</sub> where  $0 \leq i \leq 5$ , -O(CH<sub>2</sub>)<sub>j</sub>CH<sub>3</sub>, or -O(CF<sub>2</sub>)<sub>i</sub>CH<sub>3</sub> where  $0 \leq j \leq 4$ , -CN and -NH<sub>2</sub>; -CF<sub>2</sub>-; -CH<sub>2</sub>-CO-NH-CH<sub>2</sub>-; -CF<sub>2</sub>-CO-NH-CF<sub>2</sub>-; -CH<sub>2</sub>-CO-NH-CF<sub>2</sub>-; CF<sub>2</sub>-CO-NH-CH<sub>2</sub>- where  $0 \leq n$  and  $m \leq 16$ .

29. A composite according to claim 28, wherein said chain may be partially halogenated.

30. A composite according to claim 28, wherein said chain may be perhalogenated.

31. A composite according to claim 28, wherein said chain may contain thiophen units.

32. A composite according to claim 28, wherein said aromatic units may comprise constituents selected from the group consisting of:  $-(CH_2)_iCH_3$  where  $0 \leq i \leq 5$ ,  $-O(CH_2)_jCH_3$ , or  $-O(CF_2)_jCH_3$  where  $0 \leq j \leq 4$ ,  $-CN$  and  $-NH_2$ ;  $-CF_2-$ ;  $-CH_2-CO-NH-CH_2-$ ;  $-CF_2-CO-NH-CF_2-$ ;  $-CH_2-CO-NH-CF_2-$ ;  $CF_2-CO-NH-CH_2-$  where  $0 \leq n$  and  $m \leq 16$ .

33. A composite according to claim 31, wherein said thiophen units may comprise constituents selected from the group consisting of:  $-(CH_2)_iCH_3$  where  $0 \leq i \leq 5$ ,  $-O(CH_2)_jCH_3$ , or  $-O(CF_2)_jCH_3$  where  $0 \leq j \leq 4$ ,  $-CN$  and  $-NH_2$ ;  $-CF_2-$ ;  $-CH_2-CO-NH-CH_2-$ ;  $-CF_2-CO-NH-CF_2-$ ;  $-CH_2-CO-NH-CF_2-$ ;  $CF_2-CO-NH-CH_2-$  where  $0 \leq n$  and  $m \leq 16$ .

34. A composite according to claim 26, wherein X is a functional group selected from the group consisting of the acid anhydride group of  $-SH$ ;  $-SiHCl_2$ ;  $15 SiH_2Cl$ ;  $-Si(Cl)_3$ ;  $-SiHBr_2$ ;  $-SiH_2Br$ ;  $-SiBr_3$ ;  $-Si(R'(Cl)_2)$ ;  $-Si(OR')_3$ ;  $-Si(R'(OR')_2)$ ;  $-COOH$ ;  $-COCl$ ;  $-PO_3H_2$ , or  $-SO_2H$ .

35. A composite according to claim 26, wherein X is a functional group selected from the group consisting of the acid chloride group of  $-SH$ ;  $-SiHCl_2$ ;  $20 SiH_2Cl$ ;  $-Si(Cl)_3$ ;  $-SiHBr_2$ ;  $-SiH_2Br$ ;  $-SiBr_3$ ;  $-Si(R'(Cl)_2)$ ;  $-Si(OR')_3$ ;  $-Si(R'(OR')_2)$ ;  $-COOH$ ;  $-COCl$ ;  $-PO_3H_2$ , or  $-SO_2H$ .

36. A composite according to claim 26, wherein R' is an alkyl selected from the group consisting of methyl, ethyl or propyl.

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37. A composite according to claim 26, wherein said organometallic group is of the formula  $-M(Cl)_n$ .

38. A cured rubber or rubber-like composition obtained by   
30 vulcanization of a composite according to claim 1.

39. A composition according to claim 38, wherein said composition is a  
pneumatic tire.

5 40. A composition according to claim 38, wherein said composition is a  
hose.

10 41. A composition according to claim 38, wherein said composition is a  
conveyor belt.

42. A composition according to claim 38, wherein said composition is a  
pulley belt.